Carbon dioxide capture and sequestration

Techno-economic aspects of the post-combustion CO$_2$ capture processes

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With the growing awareness on global warming, carbon capture and sequestration has gained enormous importance. This report focuses attention on the various materials and methodologies available for CO$_2$ capture, particularly from stationary sources like thermal power plant emissions. The current state of development and future prospects are highlighted. The economic impact of capture technologies on the cost of power production is discussed and the way forward for their large-scale application is proposed. The primary aim of this review is to identify vital development pathways that need to be pursued to accelerate the large scale deployment of post combustion CO$_2$ capture technologies.

Keywords: Carbon dioxide capture, Post-combustion carbon dioxide capture processes, Gas-liquid absorptions, Gas-solid adsorptions, Membrane separations

Global warming has been recognized as the major factor for climate change. The contribution of carbon dioxide to this disaster is also well-known. Flue gas from stationary sources is found to be a major contributing factor for accumulation of carbon dioxide in the atmosphere. Both conventional and novel approaches have been proposed for the capture of carbon dioxide emanating from the coal fired thermal power plants. The following paragraphs illustrate the state of art of the various methods adopted for this purpose. The feasibility and the maturity levels of these technologies for commercial applications have been stressed along with the future prospects.

In modern coal fired power plants, pulverized coal is mixed with air and burnt in a boiler. The hot combustion gases exiting it generally consist of nitrogen in addition to smaller concentration of water vapor, SO$_x$, NO$_x$ and less than 15% of CO$_2$. A variety of advanced capture or separation agents are employed on this flue gas stream. Figure 1 shows a typical post combustion process flow scheme.

From an engineering viewpoint, the post combustion CO$_2$ capture (PCCC) processes can be classified as (a) gas-liquid absorption, (b) gas-solid adsorption and (c) membrane facilitated separations.

Chemical and Physical Absorption

In gas-liquid absorption, either a chemical or a physical absorbent is employed to capture and separate CO$_2$ from the rest of the flue gas stream. In the former case, CO$_2$ is chemically bound to the solvent and requires considerable energy to release it. In the latter case, CO$_2$ solubility becomes a function of pressure, temperature and the nature of solvent employed and its release is achieved through flashing the solvent at higher pressure. Liquid absorbent research is focused on development of novel systems that have more desirable CO$_2$ capture capacity, reaction rates, thermal and oxidative stabilities and decrease of regeneration energy, corrosivity, viscosity, volatility and reactivity with flue gas impurities. Figure 2 indicates the technology options available for gas-liquid absorption processes and the knowhow sources.

An efficient chemical solvent normally removes CO$_2$ from a gas stream irrespective of its

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![Fig. 1 – A typical PCCC process flow scheme.](image-url)
concentration or partial pressure and is a preferred option for post combustion CO\textsubscript{2} capture. However, its capacity is equilibrium limited and the major disadvantage lies in the higher energy requirement for its regeneration. Liquid absorbent research is focused on development of novel systems with the desired properties that are described above. The strengths and weaknesses of commercially potent liquid absorbents are highlighted in Table 1. The important chemical solvents employed for PCCC are primary, secondary, tertiary and hindered amines. They are derivatives of alcohols containing -NH\textsubscript{2} group in their chemical structure. The primary (monoethanol amine, MEA) and secondary (diethanol amine, DEA) amines react with CO\textsubscript{2} through carbamate (RNHCOO\textsuperscript{-}) and bicarbonate (HCO\textsubscript{3}\textsuperscript{-}) routes. The MEA based CO\textsubscript{2} capture systems have been in use for many years in pulverized coal based power plants established at a significant cost with a reasonable level of CO\textsubscript{2} removal efficiency. The major technology players are FLUOR, CANSOLV, MHI and WP. Since 2000,

![Image](image_url)  

**Fig. 2 – Absorption based PCCC options and the knowhow sources.**

<table>
<thead>
<tr>
<th>Absorbent</th>
<th>Application level</th>
<th>Knowhow source</th>
<th>Strengths</th>
<th>Weaknesses</th>
<th>Commercial potential</th>
</tr>
</thead>
</table>
| Alkanolamines (primary, secondary and tertiary) | Commercial | Fluor, WP, CANSOLV | • Fast mass transfer  
• Tested capability  
• Easily be retrofitted | • High regeneration energy  
• Chemical degradation  
• Corrosion | Very High |
| Sterically hindered amines | Semi-commercial | MHI | Higher CO\textsubscript{2} loading and regeneration rates | • Lower energy for regeneration | Very High |
| Inorganics K and Na carbonates | Pilot scale | Texas University, USA | • Established use in oil/gas industry  
• Favorable equilibrium  
• Less O\textsubscript{2} solubility | • Higher regeneration energy  
• Expensive | Promising |
| \(-\text{NH}_3\) & derivatives (Chilled) | Pilot scale | PSC, ALSTOM and AEP | • High CO\textsubscript{2} capacity  
• Lower heat of reaction  
• High O\textsubscript{2} tolerance  
• Simultaneous SO\textsubscript{2} and NO\textsubscript{2} reaction to form useful byproducts | • Higher volatility  
• Low temperatures (<20 °C) required  
• Higher regeneration losses | High |
| DME+PEG+MEOH (NG sweetening) | Commercial | -- | • Low regeneration heat  
• PSA and TSA for CO\textsubscript{2} release | • More suitable for high pressure operations | Low |
| NAM & NFM | Laboratory | MORPHISORB | High affinity for H\textsubscript{2}O and S compounds | • Undergo oxidative degradation | Moderate |
| Ionic liquids | Sponsored research | NETL | • Stable at high temperature  
• No gas cooling  
• Simultaneous SO\textsubscript{2} & CO\textsubscript{2} removal feasible  
• High CO\textsubscript{2} solubility | • Less regeneration energy  
• High material cost  
• Higher viscosity | Low |

**Table 1 – Performance of liquid absorbents for CO\textsubscript{2} capture in power plants**
R&D focus has been on developing high performance solvents for simultaneous removal of NOx, Hg and CO2. CANSOLV offers a CO2 capture process employing proprietary mixed amine formulations promoted with piperazine and its derivatives. They are being pilot tested in USA for natural gas and coal fired power plants. Sterically hindered amines such as 2-amino-2-methyl-1-propanol (AMP) have bulky groups attached to the nitrogen atom of the amine molecules to partially shield the amine group from the reacting acid gas. They have high potential to become leading CO2 capture agents. In 1999, Kansai Electric Power Company, Japan, and Mitsubishi Heavy Industries, Japan, commissioned a CO2 recovery plant in Malaysia employing flue gas with 8 vol.% CO2 and achieving 90 % recovery efficiency. Four commercial natural gas fired power plants equipped with PCCC facilities were subsequently commissioned, with four more under construction. The major strength of amines like MEA is their ability to react strongly with CO2 even at low CO2 concentration. The weaknesses lie in their corrosivity and relatively high regeneration energy requirement. The major challenge in utilizing amine based systems is to obtain a good trade off between lowering solvent regeneration costs and increasing the driving force needed for the main reaction.

Aqueous ammonia based PCCC technologies are endowed with lower heat of reaction as compared to amine based systems. Aqueous ammonia is in reality ammonium carbonate solution with which CO2 reacts to form bicarbonate through a reversible reaction. It has been established that the ammonia concentration has to be limited to 5 wt% and absorber temperature to 10 °C to contain vapor losses and precipitation of ammonium bicarbonate. The ability of ammonia and its derivatives to capture multiple pollutants (CO2, SO2, NOx and Mg) simultaneously make them attractive for CO2 capture from thermal power plant flue gases with minimum regeneration energy penalty. However, their higher level of volatility as compared to amines makes them susceptible to release into the flue gas stream during the absorption phase through a process called “ammonia slip”. The control of this is one of the major engineering challenges. The chilled ammonia option is basically to prevent or minimize this phenomenon. In this technology, the main trade off is between the energy required to cool the process streams and the cost of reducing the ammonia slip to acceptable levels. At present, two pilot projects are in operation in USA and Norway based on chilled ammonia process. The Power Span Corporation, USA, is developing a novel technology called ECO process, which is based on chilled ammonia and ammonium carbonate to capture CO2. Herein ammonium sulphate is obtained as a useful byproduct. Power Span Corporation, USA, employs aqueous ammonia at 25-40 °C for its 20 TPD CO2 capture facility established in collaboration with National Energy Technology Laboratory, USA (NETL). It is reported that the removal of SO2, NOx, Hg and fly ash has been achieved. The American Electric Power, USA (270 TPD) and ALSTOM, USA (35 TPD) technologies employ chilled ammonia for efficient ammonia vapor recovery and enhanced mass transfer to achieve 90 % CO2 separation. Several technological hurdles have to be overcome before these technologies are scaled-up. Intense research and development efforts are being made in this direction.

A promising alternative to chemical absorption is to employ physical solvents which can bind CO2 selectively. For natural and synthesis gas treatment for sweetening, a mixture of dimethyl ether, polyethylene glycol (PEG) and chilled methanol (-40 °C) were employed on commercial scale. The main advantage of physical adsorbents is their lower heat consumption in the regeneration step since it is driven by thermal or pressure reduction. Physical solvents are better suited for pre-combustion CO2 capture from high pressure streams in IGCC plants. Among the recently tried physical solvents, the twin morpholine solvent system (n-acetyl morpholine (NAM) and n-formyl morpholine (NFM)) has a high affinity for water, H2S and aromatic sulphur compounds. Though it does not undergo hydrolysis at higher temperatures, it can undergo oxidative degradation to other morpholine derivatives which, however, do not affect the solubility of acid gases.

Ionic liquids (ILs) are known to be selective towards CO2 absorption. In addition to their extremely low vapor pressure, they are nonflammable and exhibit high thermal stability. The mechanism of CO2 capture is generally based on physisorption involving weak interaction with CO2 molecule. Interestingly, some ionic liquids react with CO2 through a chemisorption mechanism. In view of their low heats of absorption (11 kJ/mol), they require minimum regeneration energy. ILs can also remove CO2 and SO2 simultaneously since the solubility of the latter is 8-25 times greater than that of CO2 and an
additional step is required to separate them later. Recently, task specific ionic liquids have been developed \(^1\) by introducing functional groups like amines. Polymerized ionic liquids have exhibited enhanced CO\(_2\) solubility relative to the monomeric ILs. They can be employed in facilitated transport liquid membrane systems. \(^12\) The recent developments related to reversible ionic liquids are quite interesting. \(^13\)

**Gas-solid adsorption**

Solid adsorption based PCCC processes can reduce regeneration and recirculation costs and enhance the binding capacity for CO\(_2\). They are promoted by significant gas-solid intermolecular forces. Both pressure (PSA) and temperature (TSA) swing adsorption options have been used for CO\(_2\) release. The performance of a variety of adsorbents tried for post-combustion technologies have been published, \(^16-16\) although no solid adsorbent based system has so far been employed on a commercial scale for CO\(_2\) capture. Figure 3 shows the three major types of gas-solid adsorption based PCCC processes being investigated.

**Microporous and mesoporous materials**

The kinetic diameter (the smallest effective dimension) of molecules to be separated from the flue gases varies in the narrow range of 2.65 – 3.75 Å with CO\(_2\) kinetic diameter at 3.3 Å. However, wide differences do exist in electronic properties viz., quadrupole moment and polarization of the gases in the flue gas mixture. CO\(_2\) has a large quadrupole moment of 13.4 \(\times 10^{-40}\) cm\(^2\) as compared to other gases in the mixture, promoting the separation efficiencies of meso and microporous materials like zeolites, molecular sieves, carbon nanotubes and metal organic frameworks. \(^17\) The Eni Technology based CO\(_2\) capture process employs non-volatile amines like diethanolamine and \(n, n\)-bis (2 hydroxyethyl) ethylenediamine on alumina support. \(^18\) The maximum specific CO\(_2\) capture is around 9.6 % by weight of the sorbent. Its regeneration is achieved at 100 °C under vacuum. Toshiba process employs lithium orthosilicate, which has a reaction rate five times higher than lithium zirconate. \(^19\) The reversible adsorption/desorption proceeds within 450 – 650 °C.

**Zeolites**

Zeolites are widely employed for PCCC. \(^14\) Zeolite 13X has been employed commercially using PSA at 2 bar pressure. The adsorption capacity of zeolites is greatly reduced by the presence of moisture, and therefore, necessitate very high regeneration temperatures. This is a major disadvantage of this technology. X, Y and 5A zeolites have also been reported for CO\(_2\) capture. It has been found that low SiO\(_2\)/Al\(_2\)O\(_3\) ratio and the presence of cations in the zeolite structure can enhance their adsorption capacity. The NETL process employs zeolite 13X with good potential for application in coal fired power plants. \(^20\) The Oak Ridge National Laboratory, USA, process employs carbon fiber composite molecular sieves with electric swing desorption. \(^21\)

Numerous amine modified silicon materials have been reported to improve the gas sorption properties of porous materials. \(^14-17,22\) The surface modification process has facilitated the CO\(_2\) adsorption through the formation of carbamate species and its regeneration at a lower temperature. It is interesting to note that the impregnation of polyethylenimine into MCM-41 is reported to enhance CO\(_2\) adsorption 24 folds when PSA is used. Also, metallic monolith structures coated with nanostructured hydrophobic zeolite grafted amines are being researched, for tuning CO\(_2\) binding strength by altering the alkyl chain of the amines. SO\(_2\) absorption is also possible through the use of aryl amines. \(^23\)

**Metal organic frameworks (MOF)**

MOFs are hybrid materials built from metal ions with well defined coordination geometry and organic bridging ligands. They are endowed with carefully sized cavities with high storage capacity for adsorbed CO\(_2\). Over 600 MOFs have been developed with some of them showing high CO\(_2\) capture potential. \(^24\) Further development is needed to achieve the process stability.

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Fig. 3 – Potential PCCC technologies and knowhow sources.
over thousands of cycles of operation in spite of the presence of undesirable impurities in the flue gas. The perceived advantages of MOFs include low cost, low energy consumption for regeneration, higher tolerance to impurities and attrition resistance. On a comparative basis, the active area per unit weight (m²/g) is 400-1000 for activated carbon, 1500 for zeolites and 1500-4500 for MOFs.

Zeolite imidazolate frameworks (ZIFs) constitute a subclass of MOFs that can adopt zeolite structure easily. A recent report has shown the exceptionally selective CO₂ capture and storage properties of ZIFs. Their functionalization permits the fine tuning of the interactions between their pore walls and guest molecules, thereby enhancing the adsorption selectivity. In contrast to MOFs, ZIFs exhibit high thermal and chemical stabilities under refluxing organic and aqueous media.

Carbonaceous materials

Though the surface properties of the carbonaceous adsorbents can vary widely, they are inexpensive relative to their zeolite counterparts and are least sensitive to moisture. A few studies have been reported on their use for low pressure flue gas applications using vacuum or temperature swing regeneration approaches. It is reported that the selectivity and capacity of carbonaceous adsorbents like activated carbon and charcoal are too low for post combustion CO₂ capture applications. However, in recent years, ESA of CO₂ with carbonaceous materials is gaining attention, in view of its ability to rapidly adsorb and desorb CO₂ with the application and removal of electrical charges.

Organic solids

Nanoporous self-assembled p-tert-butyl calixarenes have been employed for CO₂ capture at high pressures although they have little scope in CO₂ capture from flue gases of power plants. Covalent organic frameworks (COFs) have been tried recently for CO₂ capture at high pressure and lower temperature, but they are yet to gain technological maturity.

Supported liquid solid adsorbents

The concept of supported liquid absorbents on the porous solid substrates, is gaining importance, since it shares the benefits of high capacity of liquid amine absorbent and low regeneration energy features of solids. Current research efforts focus on overcoming or minimizing their thermal instability, fouling tendency and degradation in the presence of SO₂.

Non-porous materials

Sodium carbonate reacts reversibly with CO₂ and water to form sodium bicarbonate. This reaction is being investigated, as an inexpensive option employing TSA to regenerate the sorbent and producing nearly pure CO₂/water stream. Pilot studies based on RTI process have achieved 90 % CO₂ removal from the power plant flue gases with sorbent capacity utilization at 65 %.

Factors influencing the capacity and selectivity of solid adsorbents

The factors which contribute to high selectivity in solid adsorbents are molecular sieving, thermodynamic equilibrium, adsorbate-adsorbent material interaction and kinetic effects. The solid adsorbents have significant energy savings as compared to liquid absorbent systems since they avoid the use of a large quantity of water that must be repeatedly heated and cooled to regenerate the CO₂ capture agent. They also need less regeneration energy. The major challenges in the development of adsorption technology lie in enhancing the efficiency of heat input and output to the sorbent material, solving physical attrition problems, arresting activity deterioration of the solids over time and selection of appropriate fluid and fixed bed reaction systems and regeneration equipments. The recent comparative assessment of novel porous solid adsorbents by Hao et al. has brought out these factors quite conclusively. Table 2 lists the merits and demerits of the various solid adsorbents. Sjostrom et al. made comparative studies of solid adsorbents as a retrofit technology for CO₂ capture. They found that no adsorbent is without technical demerits even though several of them have theoretical regeneration energies significantly lower than that of globally accepted benchmarks, warranting further R&D. At present, there are no potential candidates for commercial application in the immediate future.

Membrane-based PCCC and separation

The adsorption and absorption technologies require gas-solid and gas-liquid contacting towers of large diameter (18-20 m) and length (25-30 m). Since the flue gases from power plant contain less than 15 % by volume of CO₂ and are emitted at high volumetric flow rates, membranes with as much as 1000 times
more surface area per unit volume can be more effective in comparison with the above towers. They also avoid direct contact between gas-solid and gas-liquid streams. Their advantages lie in selective extraction of CO\textsubscript{2}, low energy requirements and the configuration flexibility at plant level. However, an energy penalty has to be created for better separation through the compression of feed gas mixture. They also suffer from permeability drop due to particulate deposition on membrane surface. Table 3 highlights the merits, demerits and future potential of membrane based PCCC and separation.

### Table 2 – Performance of solid adsorbents for CO\textsubscript{2} capture

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Application level</th>
<th>Knowhow source</th>
<th>Strengths</th>
<th>Weaknesses</th>
<th>Commercialization potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zeolites (surface modified)</td>
<td>Laboratory</td>
<td></td>
<td>• CO\textsubscript{2} and SO\textsubscript{2}</td>
<td>• High regeneration temp</td>
<td>Moderate</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Capture ability</td>
<td>• Lower adsorption capacity</td>
<td></td>
</tr>
<tr>
<td>Sodium carbonate</td>
<td>Pilot scale</td>
<td>RTI, USA</td>
<td>• Low capital &amp; operating costs</td>
<td></td>
<td>Moderate</td>
</tr>
<tr>
<td>Potassium carbonate (promoted)</td>
<td>Laboratory</td>
<td>Texas University, USA</td>
<td>• Lower regeneration costs</td>
<td>• More expensive</td>
<td>Low</td>
</tr>
<tr>
<td>Metal-organic frameworks MOF</td>
<td>Laboratory</td>
<td>UOP/DOE of USA</td>
<td>• High CO\textsubscript{2} capture potential</td>
<td>• Thermal stability to be established</td>
<td>Low</td>
</tr>
<tr>
<td>Zeolite imidazolate frameworks (ZIF)</td>
<td>Laboratory</td>
<td></td>
<td>• High CO\textsubscript{2} selectivity/storage</td>
<td>• Active at higher pressures</td>
<td>Moderate</td>
</tr>
<tr>
<td>Amine enriched sorbents</td>
<td>Laboratory</td>
<td>NETL, USA</td>
<td>• Rapid desorption with electrical charge</td>
<td>• Low SO\textsubscript{2} selectivity and adsorption</td>
<td>Moderate</td>
</tr>
</tbody>
</table>

### Table 3 – Performance of membrane based PCCC and separation

<table>
<thead>
<tr>
<th>Membrane system</th>
<th>Technology level</th>
<th>Knowhow source</th>
<th>Strengths</th>
<th>Weaknesses</th>
<th>Commercial potential</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polymeric (Thin film)</td>
<td>Bench scale</td>
<td>MTR</td>
<td>• Less energy intensive</td>
<td>• Plasticization/compaction</td>
<td>Moderately high</td>
</tr>
<tr>
<td></td>
<td>(1m\textsuperscript{2} area)</td>
<td></td>
<td>• No phase changes</td>
<td>• Affected by flue gas impurities</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Improved permeability/ selectivity</td>
<td>• Degradation susceptibility</td>
<td></td>
</tr>
<tr>
<td>Inorganic (porous &amp; Nonporous)</td>
<td>Laboratory</td>
<td></td>
<td>• High temperature stability</td>
<td>• Adverse effect of steam</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• High H\textsubscript{2}/Co separation factor</td>
<td>• High operation temperatures</td>
<td></td>
</tr>
<tr>
<td>Mixed Matrices (polymer-Ceramic)</td>
<td>Laboratory</td>
<td>UNM</td>
<td>• Good H\textsubscript{2}/CO\textsubscript{2} and CH\textsubscript{4}/CO\textsubscript{2} separation factors</td>
<td>• i. Degradation due to flue gas impurities</td>
<td>Moderate</td>
</tr>
<tr>
<td>Hybrids</td>
<td>Laboratory</td>
<td>UNM</td>
<td>• Higher CO\textsubscript{2} capture efficiency</td>
<td>• Lower permeance and selectivity</td>
<td>Moderate</td>
</tr>
<tr>
<td>• Inorganic-chemical absorbents</td>
<td></td>
<td></td>
<td>• Less degradation due to impurities</td>
<td></td>
<td></td>
</tr>
<tr>
<td>• MOFs immobilized on membrane support</td>
<td>Laboratory</td>
<td>DOE, USA</td>
<td>• Exceptional H\textsubscript{2}/CO\textsubscript{2} separation</td>
<td>• Higher cost</td>
<td>Low</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Air, Water and thermal stability</td>
<td>• Stability unestablished</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Low regeneration energy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Liquid Membranes (Facilitated transport)</td>
<td>Laboratory</td>
<td></td>
<td>• Variety of carriers employable</td>
<td>• Stability not yet fully established</td>
<td>Low</td>
</tr>
</tbody>
</table>
Functionally, the membrane constituent materials can be classified as polymeric, inorganic and liquid based systems (Fig. 4).

**Polymeric membrane systems**

Polymeric membrane systems are widely employed for natural gas sweetening (CO$_2$/CH$_4$ separation). Three major challenges exist for enhancing their viability for CO$_2$ separation viz., achieving small pore sizes for selective separation, control of monomer spatial arrangement and fine-tuning of CO$_2$ interaction with the membrane matrix. The inherent advantages are less energy intensity, no process phase change requirement and low cost maintenance. Extensive reviews have been published on the merits and demerits of polymeric membrane systems.$^{16,30-32}$ Polyacetate, sulphone, carbonate, silicone and amide based membranes are amongst the most widely reported for acid gas separations. They are generally nonporous and the gas permeation occurs through solution-diffusion mechanism. The first CO$_2$ separation was attempted on cellulose acetate based membranes. However, the CO$_2$ flux of these membranes decreases substantially with time due to plasticization and compaction. Membrane Technology & Research Inc., USA, (MTR) is investigating novel thin film composite polymer membranes for CO$_2$ capture from flue gases.$^{23}$ Merkel et al.$^{33}$ evaluated the performance of MTR membrane to sequester CO$_2$ from power plant flue gases. They proposed benchmarks of CO$_2$ permeance (1000 gpu) and CO$_2$/N$_2$ selectivity (>20) to achieve economic feasibility. They developed process flow scheme for a PCCC facility for a coal fired 600 MW power plant at an estimated cost of USD 20-30/ton CO$_2$. A field site demonstration project has also been granted to MTR and its associating agencies by DOE, USA.

The polysulphone and polyimide based membranes exhibit better thermochemical and plasticization resilience coupled with mechanical strength. It is important to note that the minor components like CO, NH$_3$, H$_2$S, SO$_x$ and NO$_x$ present in flue gases from power plants can adversely impact the polymeric membrane performance. Their existence within the polymer matrix may lead to plasticization and alteration of membrane mechanical properties. The presence of water can alter both the permeability and selectivity of CO$_2$. Very little research has been done in these areas.

**Hypercrosslinked networks and mixed matrix systems**

These systems comprise aromatic rings connected to polymeric matrices through linking groups of well defined lengths to form porous networks. Modifications of the network surface could be achieved through functionalization of the precursor polymer or hypercrosslinked layer of both. Recently polyvinyl alcohol with amines has been employed for CO$_2$ separation.$^{34}$

Recently, blended polymeric membranes have been employed for CO$_2$ and N$_2$ separation.$^{35}$ The use of mixed matrix membranes comprising a heterogeneous gas separation layer with discrete inorganic/organic particles dispersed in a continuous polymeric phase has been described. The gas separation layer includes PEG, activated carbon, silica based carbonates and their mixtures. The continuous phase materials are silicone rubber and polysulphones. Functionalizing the inorganic/organic particles with amine groups is found to increase their association with continuous phase to provide better selectivity. Freeman et al.$^{36}$ incorporated various nanoparticles into polymeric membranes to significantly improve CO$_2$ permeability. Research on mixed matrix membranes is likely to be intensified in the near future due to their higher potential for CO$_2$ separation.

**Hybrid membrane systems**

The membrane based absorption systems have been employed in TNO, Kvaerner and Rite processes. The TNO process employs macroporous polypropylene membrane with aqueous alkali amine salt as the solvent. It has been reported that for large scale CO$_2$ removal and recovery, the TNO process is not commercially attractive.$^{37}$ The Kvaerner process employs PTFE membrane with aqueous MEA, MDEA and DIPA as solvents. Thus far, this technology has been focused on offshore gas production installations. No performance data is
available for CO₂ recovery from power plant flue gases. The Rite (Japan) process employs carb-polyimide membrane with high permeability and selectivity for CO₂/N₂ separation and possess a working life of 8000 h at 40 °C.

Inorganic membranes

Inorganic membranes are of porous and nonporous (dense) types suitable for high temperature operations. The mechanism of CO₂ separation in inorganic membranes is based on adsorption selectivity and surface diffusion which give rise to relatively low separation factors. Microporous silica membranes containing amine functional groups have been employed for separation of CO₂ from flue gas. The strong interaction between the permeating CO₂ molecules and the amine functional membrane pores enhances the selective diffusion of CO₂ along the membrane pore walls. The transport of other constituents viz., O₂, N₂ and SO₂ in the flue gas is simultaneously blocked.

Molecular sieve membranes

The CO₂ separation with molecular sieve membranes is based on kinetic size discrimination within the channels of the porous structure. New Mexico Institute of Mining and Technology, USA, is investigating zeolite based membranes for separation of CO₂ from flue gas at 400 °C. For high pressure natural gas sweetening, zeolite-T, DDR, silicate-1 and SAPO-34 have been employed to achieve CO₂/CH₄ selectivity based on the differences in diffusivity and competitive adsorption.

Liquid membrane systems

In liquid membrane systems, the CO₂ separation is facilitated by a preferential reversible chemical reaction between CO₂ and carriers like carbonates, amines, molten salt hydrates or ionic liquids which are immobilized in porous membranes. It has been reported that a liquid membrane system consisting of ionic liquid encapsulated in polysulphones or crosslinked Nylon 66 exhibits exceptionally high CO₂/H₂ selectivity. The cross-membrane transport is driven by the difference in the CO₂ partial pressure across the membrane. Also, ionic liquids have SO₂ solubility 8 – 25 times that of CO₂ at the same partial pressure for simultaneous removal of SO₂.

Scientific Challenges Posed by Flue Gas Impurities

The oxygen in flue gases can cause corrosion and solvent degradation. While inhibitors have been employed to mitigate these effects to a reasonable level, more robust material development still remains the key scientific challenge. SO₂ present in flue gases (300-5000 ppmv) can react irreversibly with liquid absorbents like amines to form undesirable contaminants. Though pre cleaning with limestone and other materials can reduce it to a level of 35 ppmv, further reduction to 10 ppmv level requires secondary scrubbing treatment with caustic soda solution. Added to this, at temperatures below 340 °C, SO₂ reacts with water vapor to form H₂SO₄ which will then condense to form aerosols as the flue gas is cooled. Any acid not captured during absorption will result in solvent contamination with heat stable salts. Similarly NOₓ in flue gases forms heat stable amine salts. Development of a solvent system with multi constituent capture capabilities provides the best option to tackle these problems. Fly ash present in flue gases (up to 2 grains per scf) can pose foaming problems in the absorption and stripper systems in addition to creating fouling, erosion, crevice corrosion, chemical degradation and enhanced solvent loss problems. These particulates have to be removed upstream of SO₂ scrubber. The current research efforts in solid adsorbents and membrane separators are directed towards solving the above problems.

Global R&D efforts

The global R&D activities on CO₂ capture and storage (CCS) cover scientific, regulatory, economic, political and environmental aspects. The PCCC R&D constitutes more than 30 % of research efforts followed by CO₂ sequestration (29 %), oxycombustion (20 %), pre-combustion (15 %) and CO₂ transportation (6 %). A large majority of the PCCC-R&D is devoted to coal based power generation and a significant number of adsorption and membrane based projects are in the early stages. Figure 5 shows the geographical distribution of CCS-R&D in 2009 with Asia lagging behind European Union and Americas.

The design, performance and operational aspects of amine based absorption PCCC technologies have been discussed with adequate clarity by Rao and Rubin in 2002. The Global Carbon Capture and Storage Institute, Australia, in association with the Worley Parsons, USA-led consortium consisting of Schlumberger, Baker and Mckenzie and Electric Power Research Institute (EPRI) undertook an interesting study in 2009 on the global status of CCS technologies including the functioning of R&D networks around the world. Very recently Dave and
Duffy have reported the novel developments and limitations of important CCS technologies. Folger, a specialist on Energy and Natural Resources Policy, assessed the prospects for wider scale application of PCCC technologies. Though they are capable of generating CO$_2$ capture efficiencies of 90% or more, the major drawbacks are high cost and large energy requirement for operation as well as regeneration. Kapila et al. have investigated the prospects for CCS technologies in India with the current efforts limited to laboratory level R&D.

Factors Impacting CO$_2$ Capture Efficiency

Energy penalty
The energy requirements of PCCC systems are around 10 – 100 times greater than those of other environmental control systems employed in modern thermal power plant installations. This energy penalty lowers the overall plant efficiency and increases the net cost of power generation. Folger reported typical CCS penalties for coal and natural gas based thermal power plants (Table 4). The presented data shows that the higher the plant efficiency, the smaller is the energy penalty. Innovations that enhance the efficiency of power generation can reduce the cost impact of CO$_2$ capture. The solvent regeneration contributes to highest cost component of PCCC systems.

Flue gas composition
The hot combustion gases from a coal based thermal power plant comprise mainly nitrogen, smaller quantities of water vapor and CO$_2$ formed. Besides, a variety of additional constituent’s viz., sulphur dioxide, nitrogen oxides and particulate matter also form part of flue gas. Trace quantities of mercury may also be present. Their removal may be required to provide a sufficiently clean gas stream for subsequent CO$_2$ capture.

Current Status of PCCC Technology Demonstration

Global commitments
The G8 countries in 2008 emphasized the need to accelerate the large scale CCS technology demonstration to address the global challenges of energy security, climate change and sustainable development. The uptake of CCS technologies has to be significantly advanced to reach the globally set goals, viz., 50% CO$_2$ emission reduction, its capture to exceed 10 giga tonnes/annum and its cumulative storage to reach 145 giga tonnes by the year 2050. It is estimated that 100 commercial scale technology demonstration projects are needed in coal and natural gas power plants, cement and iron/steel industries. By 2040, nearly all fossil fuel based power plants will have to employ CCS technologies.

The approximate PCCC capabilities of coal and natural gas based power projects are 150-200 MW for pilot scale, 500 MW for semi-commercial scale and >1000 MW for commercial scale demonstrations. The total global financial commitments for establishing CCS demonstration projects is around USD 130 billion till 2020 for establishing 100 projects and nearly USD 5000 billion for setting up 3400 projects by 2050. China and India have committed USD 19 billion till 2020 and >USD 1000 billion by 2050.

Commercial scale installations
The amine based CO$_2$ capture technology was patented nearly 80 years ago and since then it has been used to produce CO$_2$ as per commercial

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Plant efficiency (%)</th>
<th>Energy penalty (%)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Without CCS</td>
<td>With CCS</td>
</tr>
<tr>
<td>Subcritical powder coal</td>
<td>33</td>
<td>23</td>
</tr>
<tr>
<td>Supercritical powder coal</td>
<td>40</td>
<td>31</td>
</tr>
<tr>
<td>Natural gas combined cycle</td>
<td>50</td>
<td>43</td>
</tr>
</tbody>
</table>

$^a$Defined as added fuel input (%) per net KWH output
specifications from natural gas processing, food and beverage industries. Twelve commercial plants were established in various parts of the world for post-combustion CO\textsubscript{2} capture in thermal power plants during 1978 to 2008. Table 5 indicates their electricity generation and CO\textsubscript{2} capture capacities. Most of them partially utilize the flue gases from the power plants. Only in the case of three projects, CO\textsubscript{2} is sequestrated in deep geological formations. The oldest (1978) and largest (43 MW) CO\textsubscript{2} capture system was commissioned in USA as part of a soda ash plant. In most cases, the exact composition of amine solvent is kept as proprietary information and lies somewhere between 20 and 30%.

**Semi-commercial technology demonstration**

Since no CO\textsubscript{2} capture unit was applied to the full fuel gas stream load of a modern coal or gas fired power plant, large scale technology demonstration has become very crucial for its acceptance by the large scale user agencies as well as financial institutions worldwide. It costs nearly USD 1 billion for setting up a CO\textsubscript{2} capture facility suitable for a 400 MW thermal power plant. Ten semi-commercial scale PCCC technology demonstration projects are being established in coal based power plants in USA, Canada, Europe and Scandinavian countries. Their size varies between 60 and 1100 MW electricity generation capacity and is expected to be completed during 2014-17 (Table 6). While the end use of CO\textsubscript{2} varies, in all cases, the CO\textsubscript{2} capture technology is fully integrated into a thermal power system in order to demonstrate its viability and commercial readiness. Once the majority of the semi-commercial scale demonstration projects are successfully executed, the power generation industry will gain confidence to move forward and invest in CCS technology. Such investment would ensure continuing innovation which will ultimately help bring down capital and operating costs. The recovered CO\textsubscript{2} is also required to be stored at sufficient scale to provide necessary confidence for widespread deployment of CCS technologies.

**Pilot scale technology demonstration**

Eleven post combustion CO\textsubscript{2} capture pilot projects are currently being implemented in USA, UK, Poland, Italy, Norway, Sweden and China\textsuperscript{2} (Table 7). Only one pilot plant is integrated with a natural gas based

| Table 5 – Commercial units at thermal power plants |
|---------------------------------|-----------------|-----------------|-----------------|
| Fuel | No. of power plants | Countries | Plant capacity, (MW) | CO\textsubscript{2} capture, (MMTPA) |
| Coal | 6 | USA, Japan, China and Botswana | 8-43 | 0.05-0.29 |
| Natural gas | 6 | USA, Japan, Norway, Malaysia and Algeria | 10-18 | 0.1-0.5 |

| Table 6 – Semi-commercial demonstration projects in coal based power plants |
|---------------------------------|-----------------|-----------------|-----------------|
| Country | Number | Size (MW) | Location | CO\textsubscript{2} end use | Completion year |
| USA | 2 | 60-600 | Texas | EOR | 2014-17 |
| Canada | 3 | 110-1000 | Alberta, SKW | S,EOR | 2014-15 |
| UK | 1 | 500 | Ferrybridge | DO | 2015 |
| Poland | 1 | 858 | Belchatow | S | 2015 |
| The Netherlands | 1 | 1100 | Maasville | EGR | 2015 |
| Norway | 1 | 400* | Husnes | S,EOR | 2015 |
| Italy | 1 | 660 | Porto Tolle | S | 2015 |

| Table 7 – Pilot scale CO\textsubscript{2} capture technology demonstration plants |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Country | No. of pilot plants | Size, (MW) | Technology source(s) | CO\textsubscript{2} end use | Completion year |
| USA | 5 | 1-30 | PS,ALS,AEP, SE SM | V,S,EOR | 2008-13 |
| UK | 1 | 5 | SSE | DO | 2012 |
| Poland | 1 | 250 | PGE | S | 2014 |
| Netherlands | 1 | 20 | VF | V | 2012 |
| Norway | 1 | 0.1* | SO | S | 2011 |
| Italy | 1 | 48 | EE | EOR | 2014 |
| Sweden | 1 | 5 | EN | V | 2009 |
| China | 1 | 0.1* | HN | C | |

\textsuperscript{a} MT/Year
power plant and the rest are with coal based plants. The German pilot plant studies are mainly intended to test the PCCC technology in a near real environment at a scale that is typically one or two orders of magnitude smaller than their semi-commercial counterparts. The end use of CO\textsubscript{2} may or may not be very specific at this stage. All the above projects employ CO\textsubscript{2} capture technology by an already established gas-liquid absorption process employing amines. A pilot project set up (70 TPD coal) by Siemens in 2009 in Germany in a coal fired power plant, has achieved more than 90 % CO\textsubscript{2} capture from the flue gases. It has been shown that the flue gas scrubbing with amino acid salt solution did not affect power plant efficiency in any significant manner (less than 10 %). The process has not produced any significant CO\textsubscript{2} emission into the atmosphere. The scrubbing agent is also reported to remove other pollutants besides CO\textsubscript{2} and it can be repeatedly reused. There are reports that the National Thermal Power Corporation (NTPC) India is planning to establish a 5 MW CO\textsubscript{2} capture pilot plant in India with knowhow from Toshiba of Japan.

### Economic aspects of CO\textsubscript{2} capture

Given the worldwide interest in CCS as a potential option for climate change mitigation, the likely cost of various alternative technologies will be of great interest to policy makers. Most of the recently reported financial studies of CO\textsubscript{2} capture have been based on some of the currently developed technologies. The real challenge lies in assessing the cost components of potential future improvements, which will influence the long term competitiveness of CO\textsubscript{2} capture systems.

Finkenrath\textsuperscript{14} has reviewed and analyzed the cost factors of post-, pre- and oxy-combustion based CO\textsubscript{2} capture from coal fired, IGCC and natural gas combined cycle power sources. The present and projected future costs, their sensitivity and uncertainty were examined across a very diverse set of CO\textsubscript{2} capture installations in OECD countries during 2005-09. A snapshot of the emerging economic scenario for CO\textsubscript{2} capture from power generation plants is presented in Table 8. With the application of potential PCCC options, the cost of CO\textsubscript{2} avoided may come down to around USD 40-50 per tonne by 2030.

From economic considerations, the following are relevant:

(i) Amongst the feed stocks, coal based power plants provide the best CO\textsubscript{2} capture economics due to superior efficiencies inherent with their higher CO\textsubscript{2} content.

(ii) Early demonstration projects would cost between USD 80-120 per tonne CO\textsubscript{2} abated due to their small scale, lower efficiency and commercially non-optimized nature.

(iii) Retrofit carbon capture systems will be costlier than the newly built coal based power installations.

(iv) Currently, the differences in cost between various CO\textsubscript{2} capture options are relatively small to create scope for their pilot and semi-commercial level testing on parallel mode for the next 4-5 years.

(v) Achieving 0.4 giga tons of CO\textsubscript{2} abatement/annum may require installation of 80-120 large scale CCS projects which would typically consist of newly built power plants adjacent to retrofits and other industrial CO\textsubscript{2} capture plants, all connected to a common transport and storage network.

Rubin \textit{et al.}\textsuperscript{15} employed the learning rate approach to project the future cost of power plants with PCCC based on historical rates of change for similar technologies. The future cost trends in post combustion CO\textsubscript{2} capture technologies are evaluated in the cases of pulverized coal (PC), and natural gas combined cycle (NGCC) plants. The evaluation is also carried out for pre-combustion CO\textsubscript{2} capture technology in the case of coal based IGCC plants and oxy-fuel CO\textsubscript{2} capture process for coal fired power plants.

<table>
<thead>
<tr>
<th>Item</th>
<th>Without CO\textsubscript{2} capture</th>
<th>With CO\textsubscript{2} capture\textsuperscript{a}</th>
<th>Increase (+) or Decrease (-) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capital cost (USD/KW)</td>
<td>1899</td>
<td>3135</td>
<td>+65.0</td>
</tr>
<tr>
<td>Power output (MW)</td>
<td>582</td>
<td>545</td>
<td>-6.4</td>
</tr>
<tr>
<td>Power generation efficiency (%)</td>
<td>41.4</td>
<td>30.9</td>
<td>-25.4</td>
</tr>
<tr>
<td>Cost of electricity (USD/MWH)</td>
<td>66</td>
<td>107 (102)</td>
<td>+62.0</td>
</tr>
<tr>
<td>Cost of CO\textsubscript{2} avoided (USD/tCO\textsubscript{2})</td>
<td>--</td>
<td>58.0 (80)</td>
<td>--</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Numbers in parenthesis indicate the average figures for natural gas based power plants
plants. The results of this study when projected at 100 GW installed capacity indicates the following:

(i) A 3-5% decrease in electricity cost for each doubling of capacity.

(ii) The largest reduction of 18% in electricity cost is seen in IGCC system and the smallest of 10% for the oxy-fuel system on doubling the installed capacities.

Timescale for the development and commercialization of PCCC technologies

International experts on PCCC technologies feel that at least 20 large scale (>1 million TPA) carbon capture projects are needed at different power plants to validate operational reliability, capital investment and operational costs with different fuels, extent of carbon capture and feasibility of geological storage media. Both coal and gas based power plants need to be covered. From the engineering perspective, the validation of integrated plant design, its effectiveness and reliability of control systems under steady state and transient conditions and startup/shutdown strategies are vital factors to be studied.

For fixing an appropriate time scale for technology development as well as demonstration components, the time frame normally required for each of the following activities need to be identified as: TD1: Bench scale proving (component wise); TD2: Pilot level scale-up (component wise); TD3: Semi-commercial technology demonstration (semi-integrated); TD4: Full scale commercial deployment (integrated). It is also necessary to identify parallel and sequential process options based on the current and medium term R&D outcomes. In the highly research intensive area of CO₂ capture, several parallel development activities may have to be pursued with provision for intensifying technology scale up and demonstration activities when highly positive results are obtained during a particular R&D phase. Figure 6 shows the time scale required for an aggressive development schedule for adsorption and membrane based PCCC technologies up to semi-commercial scale. Such a schedule will facilitate demonstration of PCCC technologies from 2022 onwards for setting up large scale commercial installations.

Conclusions

The commercial success of PCCC is mostly technology driven. At present, there is lack of large scale demonstration capabilities for any technology other than those based on amine and ammonia absorption in thermal power plants. Most of the adsorption and membrane based technological options are still in early R&D stage and a credible estimate of their success or failure is difficult to provide at the current stage of development. Even in the case of amine and ammonia based PCCC technologies, several commercial and semi-commercial ventures which were found to be successful initially, their use declined by more than 50% after more than a decade of deployment at coal fired power plants due to insurmountable techno economic factors. This trend emphasizes the need to intensify parallel R&D efforts on other potential alternatives based on super adsorbents and novel membranes and undertake pilot and semi-commercial level scale-up initiatives on fast track. Special attention has to be given to hybrid absorption-adsorption/membrane separation systems that can provide highly impressive CO₂ capture efficiency and selectivity. Past experiences have shown that adsorption-diffusion processes have a strong influence on the pace of innovation and enhance the prospects for cost effective PCCC technologies.

As far as economic factors are concerned, in the case of amine based PCCC technologies, fairly good confidence has been generated in recent years to continuously bring down the unit cost of CO₂. In all other cases, the cost figures are yet to reach commercially viable levels.

References

4 Carbon Storage Core R&D; http://www.netl.doe.gov/technologies/carbond_seq/corerd/corerd.html.